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(54) Title: SIZING EMULSION

(57) Abstract: The invention refers to a novel sizing emulsion comprising a substituted succinic anhydride and positively charged colloidal silica particles or positively charged colloidal aluminia particles or positively charged colloidal zirconia particles.

Sizing emulsion

The present invention relates to an aqueous sizing emulsion and more specifically to emulsions containing a substituted succinic anhydride as sizing agent, commonly referred to as ASA, and positively charged colloidal cationic silica particles, positively charged colloidal aluminia particles or positively charged colloidal zirconia particles.

Aqueoùs emulsions of substituted succinic anhydrides are used for sizing of neutral to slightly alkaline stocks at which pH range calcium carbonate effectively can be used as filler material. As substituted succinic anhydrides are hydrophobic, the size has to be evenly distributed in an aqueous phase before being added to the cellulosic stock. Usually such sizing emulsions are prepared in the vicinity of the end user, i.e. in the paper mill, in the presence of surfactants and/or polyelectrolytes such as starches.

Substituted succinic anhydrides generally provide satisfactory sizing of the paper. Though, sizing properties of substituted succinic anhydrides commonly deteriorates with cellulosic stocks having a high conductivity due to a high amount of charged particles and/or stocks having a significant amount of dissolved organic substances, i.e. lipophilic wood extractives, such as resin acids, fatty acids, fatty esters, etc. High conductivity stocks and/or stocks containing dissolved organic substances are even more pronounced in paper mills where the white water is extensively recirculated with the introduction of only minor amount of fresh water into the process, thereby increasing the amount of conductivity and the accumulation of organic substances/lipophilic extractives and non-retained sizing agents in the white-water and the stock to be dewatered.

Moreover, intimately linked with the high reactivity of succinic anhydride-based sizing agents are problems with deposits in the paper-making machine due to hydrolysed sizing material. Problems which are accentuated when recirculating the white water.

Furthermore, it is desirable to further improve sizing properties of substituted succinic anhydride size emulsions.

WO-A1-9731152 refers to sizing emulsions comprising a reactive sizing agent and an anionic microparticulate material rendering the emulsion anionic. Furthermore, it is stated that the inclusion of cationic compounds is undesirable, thus, the sizing dispersions are essentially free from cationic compounds.

From EP-A1-564994 it is known to use sizing compositions comprising a ketene dimer and positively charged compounds. When using ketene dimers as sizing agent the slipperiness of the surface of the produced paper is increased. The object of the compositions of EP-A1-564994 is to increase the coefficient of friction of the paper surface However, by using a substituted succinic anhydride the problem of slipperiness is circumvented due to the fact that substituted succinic anhydride sizing agents do not introduce slipperiness to the paper surface. Furthermore, ketene dimer sizing agents are slow reacting sizes compared to

substituted succinic anhydrides based sizing agents making it impossible to achieve full sizing on the paper machine. Accordingly, paper sized with ketene dimer needs to be post-cured at ambient temperatures before being used in printing processes.

WO 9617127 relates to an anionic sizing dispersion comprising a cellulose-reactive sizing agent and anionic colloidal aluminium-modified silica particles, however, positively charged silica particles are not disclosed.

WO 9833979 discloses a sizing dispersion of a cellulose-reactive sizing agent and a dispersing system containing cationic organic compound and an anionic colloidal particle.

In accordance with the present invention it has been found that improved sizing characteristic can be obtained with aqueous emulsions according to the claims. More specifically, the invention provides an aqueous emulsion comprising substituted succinic anhydride and positively charged colloidal silica particles, positively charged colloidal aluminia particles or positively charged colloidal zirconia particles. Additionally, the invention provides a process for the production of cellulose-based products wherein an aqueous sizing emulsion is added to a cellulosic suspension or a dewatered cellulosic suspension.

The present size emulsion makes it possible to produce paper with improved sizing over conventional size emulsions at a corresponding dosage and to use a lower dosage of substituted succinic anhydride sizing agent to attain a corresponding level of sizing. The possibility of using lower amounts of sizing agent to obtain in-specific sizing reduces the risk of accumulation of non-adsorbed sizing agents in the white water recirculating in the process, thereby reducing the risk of aggregation and deposition of the sizing agent on the paper machine.

Starch cannot be used in emulsions without being pretreated by cooking, a treatment which greately affect the properties of starch. Accordingly, it is important how the cooking is implemented in order to obtain a starch with adequate characteristics. Furthermore, there is always a possibility that the level of bacterial activity may increase in cooked starch impairing the properties. It is therefore desirable to be able to reduce the amount of starch or even omit starch in sizing emulsions of ASA.

It is also desirable to facilitate the emulsification of the sizing agent by the preparation of the emulsion in the presence of one compound acting both as dispersing agent and stabilising agent, which enables a simplified preparation at the end user.

The sizing agent comprised in the emulsion of the present invention is a substituted succinic anhydride, commonly referred to as ASA. Suitable acid anhydrides can be characterized by the general formula (I) below, wherein R^1 and R^2 can be identical or different and represent saturated or unsaturated hydrocarbon groups suitably containing from 8 to 30 carbon atoms, or R^1 and R^2 together with the -C-O-C- moiety can form a 5 to 6

membered ring, optionally being further substituted with hydrocarbon groups containing up to 30 carbon atoms. Examples of acid anhydrides which are used commercially include alkyl and alkenyl succinic anhydrides such as isooctadecenyl succinic anhydride. Further examples include iso-octadecyl succinic anhydride, n-hexadecenyl succinic anhydride, dodecenyl succinic anhydride, decenyl succinic anhydride, octenyl succinic anhydride, triisobytenyl succinic anhydride, 1-octyl-2-decenyl-succinic anhydride and 1-hexyl-2-octenyl-succinic anhydride.

$$\text{(I)}\quad R^1 - \overset{\overset{\displaystyle O}{\|}}{C} - O - \overset{\overset{\displaystyle O}{\|}}{C} - R^2$$

Suitable acid anhydrides include the compounds disclosed in US 3102064, US 3821069, US 3968005, US 4040900 and Re 29960 which are incorporated herein by reference. The emulsion may contain one or a mixture of different substituted succinic anhydride(s).

The sizing emulsion according to the present invention further comprises positively charged colloidal silica particles, positively charged colloidal aluminia particles or positively charged colloidal zirconia particles. Stable cationic aquasols of colloidal silica, alumina, or zirconia are well known in the art, for example from US 3007878, US 3620978, US 3719607 and US 3956171 which all are incorporated herein by reference. Suitably, these sols contain colloidal, dense, finely divided particles.

Preferably, positively charged colloidal silica particles, also referred to as colloidal cationic silica particles, are contained in the emulsion. Usually, the colloidal silica particles are provided as aquasols. Typical known sols are those containing positively charged particles having suitably a dense silica core coated/modified with the same or different polyvalent metal- oxygen compounds including metal oxides, metal hydroxides and hydrated metal oxides. Preferably, the silica particles are coated with one polyvalent metal-oxygen compound, suitably with tri- and tetravalent metal-oxygen compound such as aluminium, chromium, gallium, titanium and zirconium, whereby aluminium is especially preferred. Suitable anionic counter ions include halides such as chloride, acetate or nitrate. Suitably, the positively charged colloidal silica particles are inorganic silica particles which may be surface-modified, preferably with aluminium such as various oxides and hydroxides of aluminium.

The positively charged silica particles can have a particle size less than about 500 nm and usually greater than 1.0 nm. Preferably, the positively charged silica preferably has a average particle size below 100 nm and generally in the range of from 2 nm up to 100 nm,

suitably in the range from 2 nm up to 80 nm, and preferably in the range from 2.5 nm up to 50 nm. The specific surface area of the silica particles can be in the range of about 5 to about 1800 m^2/g, suitably in the range of from about 30 to about 1200 m^2/g and more preferably from 50 to 1000 m^2/g. The specific surface area can be measured, after removal of the polyvalent metal, by means of titration with NaOH in conventional manner, for example according to the method described by Sears in Analytical Chemistry 28(1956):12, 1981-1983.

The positively charged colloidal aluminium-modified silica particles preferably have a weight ratio of Al_2O_3 to SiO_2 in the range from 1:20 up to 4:1, suitably from 1:10 up to 2:1 and most preferably in the range from 1:5 to 1:1.

The general method for preparing positively charged cationic silica sols starts suitably from aqueous sols of silica which are reacted with a basic salt of a polyvalent metal to give the sol particles a positive surface charge and stabilisers such as boric acid, alkali metal bases, alkaline earth metal bases, ammonia etc. The polyvalent metal salt is usually an aluminium salt, however, it is also possible to use basic salts of other polyvalent metals for preparing cationic silica based sols, such as those mentioned above. Suitably, any basic salt which is water soluble and renders the desired positively charged surface can be used and typically the cationic silica is prepared using chlorides, nitrates or acetates of the metal. Preferably, poly aluminium chloride is used as basic salt.

According to one preferred embodiment of the present invention the aqueous emulsion comprises a substituted succinic anhydride and positively charged colloidal silica particles which are defined above.

According to yet another preferred embodiment the emulsion consists essentially of a substituted succinic anhydride and positively charged colloidal silica particles, positively charged colloidal aluminia particles or positively charged colloidal zirconia particles. Suitably, the emulsion consists essentially of substituted succinic anhydride and positively charged colloidal silica particles. By the wording "consists essentially of" is meant that the emulsion may comprise small amounts of other compounds such as emulisifiers and stabilisers, suitably less than 5 weight %, preferably less than 1 weight % based on total aqueous emulsion.

The emulsions according to the invention can have contents of substituted succinic anhydride sizing agents from about 0.1% by weight up to about 50% by weight based on total emulsion. The content of substituted succinic anhydrides sizing agent is suitably within the range of from 1 up to 40% and preferably from 2 up to 30% by weight.

In the emulsions according to the invention the weight ratio of substituted succinic anhydride sizing agent to the total amount of positively charged colloidal particles, preferably positively charged colloidal silica particles, can be in the range of from 1:1 up to 100:1. The

weight ratio is suitably in the range from 1.5:1 up to 30:1 and preferably in the range from 2:1 up to 20:1. The solids content of the emulsions preferably exceeds 1% by weight and can reach 50% by weight. The solids content suitably exceeds 5% by weight. The upper limit is suitably 40% and preferably 30% by weight.

Preferably, the overall charge of the aqueous emulsion of the present invention comprising colloidal particles and optional protecting colloids and/or emulsifying agents is cationic.

If desired, non-ionic, anionic, amphoteric or cationic protective colloids and non-ionic, amphoteric or cationic dispersing agents may be included in the emulsions, preferably in minor amounts and provided that the overall charge of the total amount of colloidal silica particles and/or optional protective colloids and/or dispersing agents which are present in the dispersions is positive or cationic. Such compounds, i.e. dispersing agents, can advantageously be included in emulsions of higher dry contents. As examples of suitable protective colloids can be mentioned water-soluble cellulose-derivatives such as hydroxy-ethyl- and hydroxypropyl-, methylhydroxypropyl- and ethylhydroxyethylcellulose, methyl- and carboxymethylcellulose, gelatin, starch, guar gum, xanthan gum, polyvinyl alcohol, etc.. Non-ionic dispersing agents can for example be selected from ethoxylated fatty alcohols, fatty acids, alkyl phenols or fatty acid amides, ethoxylated or non-ethoxylated glycerol esters, sorbitan esters of fatty acids, etc.. Suitable cationic dispersing agents and protective colloids can for example be selected from nitrogen-containing compounds such as quaternary ammonium compounds, salts of tertiary amines, water-soluble nitrogen-containing epichlorohydrin resins and cationic starches, etc.. The emulsion may also contain other additives such as preservative agents.

The emulsions according to the invention can preferably be prepared by simply mixing a substituted succinic anhydride sizing agent with a sol of positively charged colloidal particles described above.

The emulsions according to the invention can be used in a conventional manner in the production of cellulose-based products, including paper, board and cardboard. They can be used both for surface sizing and internal or stock sizing. The present invention also relates to a process for the production of cellulose-based products adding an aqueous emulsion containing a substituted succinic anhydride sizing agent and colloidal cationic particles, as those defined above, to a cellulosic suspension or a dewatered cellulosic suspension. The stock/suspension contains cellulosic fibres, optionally in combination with mineral fillers, and usually the content of cellulosic fibres is at least 50% by weight, based on dry stock. Examples of fillers of conventional types include kaolin, china clay, titanium dioxide, gypsum, talc and natural and synthetic calcium carbonates such as chalk, ground marble and precipitated calcium carbonate. The method is of course advantageous to the

papermaker in that the sizing dispersion has high sizing efficiency which reduces the tendency of the sizing agent to form deposits and thus simplifies high shearing operations such as pumping and dosing. Suitably, the amount of sizing agent either added to the stock containing cellulose fibers, and optional fillers, or applied on the cellulose-based product as a surface size, usually at the size press, is from 0.01 to 1.0% by weight, based on the dry weight of cellulose fibers and optional fillers, preferably from 0.05 to 0.5% by weight, where the dosage is mainly dependent on the quality of the pulp or cellulose-based product to be sized, the substituted succinic anhydride sizing agent used and the level of sizing desired.

Chemicals conventionally added to the stock in papermaking such as retention aids, aluminium compounds, dyes, wet-strength resins, optical brightening agents, etc., can of course be used in conjunction with the present emulsions. Examples of aluminium compounds include alum, aluminates and polyaluminium compounds, e.g. polyaluminium chlorides and sulphates. Examples of suitable retention aids include cationic polymers, anionic inorganic materials in combination with organic polymers, e.g. bentonite in combination with cationic polymers, silica-based sols in combination with cationic polymers or cationic and anionic polymers. Particularly good stock sizing can be obtained when using the dispersions of the invention in combination with retention aids comprising cationic polymers. Suitable cationic polymers include cationic starch, guar gum, acrylate-based and acrylamide-based polymers, polyethyleneimine, dicyandiamide-formaldehyde resins, polyamines, polyamidoamines and poly(diallyldimethyl ammoniumchloride) and combinations thereof. Cationic starch and cationic acrylamide-based polymers are preferably used, either alone or in combination with each other or with other materials. In a preferred embodiment of the invention, the emulsions are used in combination with a retention system comprising at least one cationic polymer and anionic silica-based particles such as retention systems sold under the name COMPOZIL®. The present emulsions can be added before, between, after or simultaneously with the addition of the cationic polymer or polymers. It is also possible to pre-mix the size emulsion with a retention aid, e.g. a cationic polymer like cationic starch or a cationic acrylamide-based polymer, prior to introducing the mixture thus obtained into the stock.

The invention is further illustrated in the following examples, which, however, are not intended to limit the same. Parts and % relate to parts by weight and % by weight, respectively, unless otherwise stated.

In the following examples the $cobb_{60}$-test and the Hercules Sizing Test (HST) has been used to evaluate the sizing performance. A higher value when using the HST test indicates better sizing, whereas a low value when using the $cobb_{60}$-test indicates improved sizing.

Example 1

The sizing efficiency of the novel emulsion was evaluated in this example using a standard HST test on paper with a grammage of 78 g/m^2. To a furnish of birch and pine kraft pulp (60:40 weight %) with a consistency of 0.5% containing 20 weight % calcium carbonate based on dry fibres having a conductivity of 520 μS/cm and a COD value of 15 mg/l the novel emulsion comprising alkenyl succinic anhydride to positively charged aluminium-modified colloidal silica particles in a weight ratio of 15:1 was added at an amount of 2 kg/ton dry pulp based on ASA (test 1 and 2). The used retention system contained cationic starch with a D.S. of 0.035 and anionic silica sol. For comparison sizing efficiency of prior art emulsions comprising alkenyl succinic anhydride (ASA) and a cationic starch were evaluated (test 3 and 4) having a weight ration ASA to starch of approximately 2,7:1. The prior art emulsions were added at an amount of 2 kg/ton dry solids based on ASA.

Table 1

Emulsion	Cationic starch* kg/ton	Anionic silica sol* kg/ton	ASA kg/ton	HST
Test 1, novel emulsion	10	1	2	318
Test 2, novel emulsion	10	0.5	2	257
Test 3, prior art emulsion	9	1	2	223
Test 4, prior art emulsion	12.5	1	2	201

* retention system

Obviously, an emulsion according to the present invention shows significantly higher sizing values than the prior art emulsions.

Example 2

In this example the sizing efficiency (Cobb$_{60}$ –test) of the novel emulsion was evaluated using the same furnish as in example 1, however, with a conductivity of 508 μS/cm. The retention system used contained a cationic polyacrylamide of medium molecular weight with 10% charge and an anionic bentonite. All emulsions contained alkenyl succinic anhydride as sizing agent and the amount of added sizing agent was 2kg/ton dry pulp based on ASA. The emulsion used in test 1 was in accordance with the invention comprising colloidal cationic aluminium modified silica particles and ASA in a weight ratio

of 1:10. The emulsion in test 2 was according to prior art comprising anionic silica particles and ASA in a weight ratio of 1:10. The emulsion in test 3 comprised anionic bentonite and ASA in a weight ratio of 1:10.

Table 2

Emulsion	Cationic polyacrylamide* kg/ton	Bentonite* kg/ton	ASA kg/ton	$Cobb_{60}$
Test 1	0,5	2,0	2,0	35
Test 2	0,5	2,0	2,0	100
Test 3	0,5	2,0	2,0	81

* retention system

Table 2 shows that an emulsion containing positively charged colloidal silica particles has excellent sizing properties compared to emulsions containing anionic particles.

Example 3

In this example the sizing efficiency of the novel emulsion was evaluated by using the $Cobb_{60}$–test. The furnish was a bleached mechanical pulp with higher amounts of dissolved organic substances (organic trash) and with a concentration of 0.5% based on dry fibres, a conductivity of 503 µS/cm and a COD value of 65 mg/l. The retention system contained cationic starch and anionic silica sol. The emulsion in test 1 according to the invention contained ASA and colloidal positively charged aluminium modified silica particles in a weight ratio of 6.7:1. The emulsion in test 2 according to prior art contained ASA and cationic starch in a weight ratio of 2.7:1. All emulsions were prepared with the same ASA sizing agent and added to the furnish in an amount of 2.0 kg/ton dry pulp based on ASA.

Table 3

Emulsion	Cationic starch* kg/ton	Anionic silica sol* kg/ton	ASA kg/ton	$Cobb_{60}$
Test 1	10	1.0	2	29
Test 2	10	1.0	2	84

*retention system

Table 3 surprisingly shows that good sizing results are obtained when the emulsion according to the invention is used on a furnish with higher amounts of dissloved organic substances.

Claims

1. Aqueous sizing emulsion, c h a r a c t e r i s e d in that the emulsion comprises substituted succinic anhydride and positively charged colloidal silica particles or positively charged colloidal aluminia particles or positively charged colloidal zirconia particles.

2. Aqueous sizing emulsion, c h a r a c t e r i s e d in that the emulsion comprises substituted succinic anhydride and positively charged colloidal silica particles.

3. Sizing emulsion according to any of the preceding claims c h a r a c t e r i s e d in that the silica particles are modified with at least one polyvalent metal.

4. Sizing emulsion according to any of the preceding claims, c h a r a c t e r i s e d in that the silica particles are aluminium-modified.

5. Sizing emulsion according to claim 4, c h a r a c t e r i s e d in that the weight ratio of Al_2O_3 to SiO_2 of the silica particles is in the range from 1:20 up to 4:1.

6. Sizing emulsion according to any of the preceding claims, c h a r a c t e r i s e d in that the weight ratio of substituted succinic anhydride to the total amount of positively charged colloidal particles is in the range of from 1:1 to 100:1.

7. Sizing emulsion according to any of the preceding claims , c h a r a c t e r i s e d in that the colloidal silica particles have a size less than 500 nm.

8. Sizing emulsion according to any of the preceding claims, c h a r a c t e r i s e d in that the silica particles have a specific surface area in the range from 5 up to 1800 m^2/g.

9. Sizing emulsion according to any of the preceding claims, c h a r a c t e r i s e d in that the substituted succinic anhydride is present in an amount of from 0.1% by weight to 50% by weight based on total emulsion.

10. Sizing emulsion according to any of the preceding claims, c h a r a c t e r i s e d in that the substituted succinic anhydride is alkenyl succinic anhydride.

11. Use of an aqueous sizing emulsion according to any of the preceding claims for stock sizing or surface sizing of cellulose-based products.

12. A process for the production of cellulose-based products, wherein an aqueous emulsion according to claims 1-10 is added to a cellulosic suspension or a dewatered cellulosic suspension.